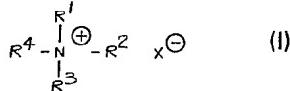

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(54) Process for the Preparation of Concentrated Solutions of Dyestuffs and of Brighteners

(57) Process for the preparation of concentrated aqueous solutions of dyestuffs and of brighteners, the inorganic salts being separated off and the sodium salts, potassium salts and alkaline earth metal salts of the dyestuffs and the chlorides, sulphates and methosulphates in the case of cationic dyestuffs being converted into salts which are more readily soluble, without the free acids or bases being intermediately isolated, characterised in that the inorganic salts are separated off by means of a membrane separation process and, before, during or after separating off the inorganic salts originally present, 10—500 mol%, relative to the dyestuff, of ammonium salts of the formula I



wherein

R¹, R², R³ and R⁴ denote hydrogen, alkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl, —(C₂H₄O)_n—H, —(C₃H₆O)_n—H, —[CH₂—CH(CH₂OH)O]_n—H or —[CH₂—CH(CH₂OH)—CH₂O]_n—H, or two of the radicals R¹, R², R³ and R⁴, together with the N atom and optionally further hetero-atoms, denote a saturated heterocyclic ring, alkyl or alkoxy containing 1 to 20 C atoms,

n denotes a number from 2 to 20 and

X[⊖] denotes the anion of an inorganic acid or OH[⊖], or lithium salts are added in the case of anionic dyestuffs and brighteners, and 10—500 mol%, relative to the dyestuff, of salts of cyclic or acyclic organic acids containing, as the cation, the cation of an inorganic base are added in the case of cationic dyestuffs and brighteners, and concentrated solutions obtained by this process and their use for dyeing natural or synthetic fibre materials.

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SPECIFICATION**Process for the Preparation of Concentrated Solutions of Dyestuffs and of Brighteners**

- The present invention relates to a process for 5 the preparation of concentrated aqueous solutions of dyestuffs and of brighteners from ionic dyestuffs, in which the sparingly soluble dyestuff salts are largely freed from the inorganic salts, and are converted into dyestuff salts which 10 are more readily soluble, by means of a membrane separation process and with the addition of an ionic compound.
- DT-AS (German Published Specification) 2,204,725 describes the preparation of dyestuff 15 solutions by pressure permeation, the inorganic salts being removed. The cations of the dyestuff salts or brightener salts remain unchanged. They are usually sodium ions, potassium ions or alkaline earth metal ions.
- 20 If such solutions of dyestuffs or brighteners are then concentrated, for example by pressure permeation, the maximum concentration is given by the limit of the solubility of the dyestuff salt or brightener salt.
- 25 It is indeed known that anionic dyestuffs in the form of the amine salts and cationic dyestuffs as salts of organic acids are in most cases more suitable for the preparation of concentrated solutions, but unless such salts are obtained 30 directly during production of the dyestuff, they could hitherto be prepared only with difficulty (for example DT-OS (German Published Specifications). 1,719,396 and 2,209,478 and German Patent Specification 2,115,877).
- 35 It has now been found, surprisingly, that the inorganic salts can be separated off and the sodium salts, potassium salts and alkaline earth metal salts of the dyestuffs in the case of anionic dyestuffs and brighteners and the chlorides, 40 sulphates and methosulphates of cationic dyestuffs and brighteners can be converted into salts which are more readily soluble in a simple and elegant manner without the free acids or bases or other derivatives being intermediately 45 isolated when the inorganic salts are separated off by means of a membrane separation process and, before, during or after separating off the inorganic salts originally present, 10—500 mol%, relative to the dyestuff, of ammonium salts of the 50 formula



wherein

- R¹, R², R³ and R⁴ denote hydrogen, alkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl, 55 —(C₂H₄O)_n—H, —(C₃H₆O)_n—H, —[CH₂—CH(CH₂OH)O]_n—H or —[CH₂—CH(CH₂OH)—CH₂O]_n—H, or two of the radicals R¹, R², R³ and R⁴, 60 together with the N atom and optionally further hetero-atoms, denote a saturated

heterocyclic ring, alkyl or alkoxy containing 1—20 C atoms,

- n denotes a number from 2 to 20 and X[⊖] denotes the anion of an inorganic acid or OH[⊖], or of lithium salts are added in the case of anionic dyestuffs and brighteners, and 10—500 mol%, relative to the dyestuff, of salts of cyclic or acyclic organic acids containing, as the cation, the cation of an inorganic base are added in the case of cationic dyestuffs and brighteners.
- Examples of suitable anions X[⊖] of the ammonium salts of the formula (I) are chloride, 75 sulphate, bromide, carbonate or phosphate.
- Examples of suitable saturated heterocyclic rings which two of the radicals R¹, R², R³ and R⁴ can form, together with the N atom, are piperidine, piperazine and morpholine.
- 80 Examples of suitable lithium salts are lithium chloride, carbonate, oxide and sulphate.
- Preferred ammonium compounds of the formula I are those which have a molecular weight the same or greater than the molecular weight of the particular dyestuff and/or are predominantly held back by the membrane used.
- The water-soluble anionic dyestuffs and brighteners which can be used according to the invention are, in particular, those with sulphonic acid groups, carboxylic acid groups and sulphonamide groups, and metal complex dyestuffs. In this context, there may be mentioned the alkali metal salts and alkaline earth metal salts of acid dyestuffs for wool, of reactive 95 dyestuffs, of acid dyestuffs for polyamide, of metal complex dyestuffs and of direct dyestuffs for cotton, which can belong to the azo, anthraquinone and phthalocyanine series.
- Examples of anionic optical brighteners which can 100 be used according to the invention are derivatives of the stilbene, coumarin, pyrazine, pyrazoline, oxazine, oxazolyl, imidazolyl and naphthalic acid imide series.
- The process according to the invention is 105 particularly suitable for the preparation of solutions of stilbene-azo and stilbene-azoxy dyestuffs, such as are described, for example, in German Patent Specifications 38,735, 883,024 and 922,123, and in the Colour Index under the 110 structure numbers 40,000 to 40,006, 40,015, 40,025, 40,030, 40,045, 40,050, 40,055, 40,065, 40,066, 40,070, 40,205, 40,210, 40,215, 40,220, 40,225, 40,230, 40,235, 40,240, 40,245, 40,260, 40,265, 40,270, 115 40,275, 40,290, 40,291, 40,295, 40,500, 40,505 and 40,510.
- In the case of the azo dyestuff series, the process according to the invention is particularly suitable for the preparation of solutions of 120 dyestuffs which contain sulfo groups and a urea group.
- Examples of water-soluble cationic dyestuffs which can be used according to the invention are the salts and metal halide double salts of methine 125 dyestuffs and azamethine dyestuffs, which can contain the most diverse heterocyclic rings, as

well as dyestuffs of the diphenylmethane, triphenylmethane, oxazine, thiazine and 1,2-pyrone series and dye salts of the arylazo and anthraquinone series with an external onium

- 5 group. The cationic optical brighteners can belong to the same classes of substances as the anionic optical brighteners already mentioned, and contain amine or ammonium groups.

Examples of suitable onium groups are

- 10 ammonium and hydrazinium.

Examples of suitable cyclic and acyclic organic acids, the inorganic salts of which can be reacted with the cationic dyestuffs and brighteners, are aliphatic or aromatic monocarboxylic or

- 15 polycarboxylic acids and monosulphonic or polysulphonic acids, which can be substituted by hydroxyl, halogen, C₁—C₄-alkoxy, nitro, amino, C₁—C₄-alkyl (in the case of an aromatic acid), cyano or oxo groups, and furthermore CH-acid

- 20 compounds, such as acetoacetic acid esters, especially the C₁—C₄-alkyl esters. Formic acid and acetic acid are particularly suitable.

The organic acids are preferably employed as the alkali metal salts or alkaline earth metal salts,

- 25 especially as the sodium salts or potassium salts.

Examples of suitable cations of inorganic bases of the salts of organic acids are the cations of the alkali metals and alkaline earth metals, especially of potassium, sodium and calcium.

- 30 The ionic compounds rendering the dyestuff or brightener more readily soluble are preferably added after removal of the inorganic salts originally present. This prior desalination is preferably carried out at pH 1—5 in the case of

- 35 anionic dyestuffs and brighteners and at pH 9—13 in the case of cationic dyestuffs and brighteners. The membrane separation process is continued in order to likewise separate off inorganic salts newly formed by the salt-to-salt

- 40 conversion and in order to subsequently concentrate the dyestuff solution or brightener solution up to the desired final concentration.

Membrane processes which can be used in the sense of this invention are reverse osmosis,

- 45 ultrafiltration, dialysis and electrodialysis.

Such membrane processes are described in detail, for example, in U.F. Franck, Dechema-Monographie 75, (1974), 1,452—1,485 9/37.

Membranes which can be used for pressure

- 50 permeation, that is to say ultrafiltration and reverse osmosis, and for dialysis are those of cellulose or cellulose diacetate or triacetate, or those of synthetic polymers, such as polyamides, polyolefines, polysulphones and many others.

- 55 Furthermore, however, those of porous glass or heavy metal oxides can also be used. The latter are known as dynamic membranes.

So-called ion exchange membranes such as are described in W. Pusch, Chemie-Ingenieur-

- 60 Technik 47 (1975) 22 914—925, can be used for electrodialysis and also for pressure permeation and dialysis.

The pressure permeation is preferably carried out at pressures between 0.5 and 60 bars using

- 65 pore diffusion membranes or solution diffusion membranes.

Those membranes which predominantly, preferably to the extent of over 90%, hold back the dyestuff are employed.

- 70 The pH value and the temperature are not critical for carrying out the membrane separation process, since suitable membranes are available for all pH ranges and temperature ranges.

The aqueous solutions obtained by the process

- 75 according to the invention have a content of more readily soluble salts, according to the definition of this application, of 10—40% by weight, preferably 10—30% by weight, and, in addition to water, can also contain up to 30% by weight of,

- 80 ammonium compounds of the formula (I) or of salts of cyclic and acyclic organic acids, the % by weight relating to the total weight of the solution.

Customary additives, such as urea, dextrin, glucose or ethylene glycol, can also be added to 85 the solutions prepared by the process according to the invention.

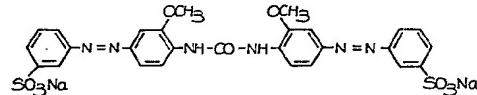
Such solutions are distinguished by high stability on storage between 0—40°C and by convenient use, the dyestuff solutions and

- 90 brightener solutions are suitable for the preparation of dyebaths and printing pastes for dyeing and printing natural and synthetic fibre materials, for example those of wool, silk, leather, polyamide, acid-modified polyester,

- 95 polyacrylonitrile and cellulose, especially paper.

Example 1

50 kg of the solution obtained after the preparation of the dyestuff of the formula



- 100 with a solids content of 3% and a sodium chloride content of 120% by weight, relative to the dyestuff, is subjected to diafiltration with 100 kg of water on a reverse osmosis pilot plant apparatus which has a membrane area of 0.36 m²

- 105 and is fitted with a cellulose acetate membrane with a nominal separation limit of MW 500 and a sodium chloride retention of 30%. The diafiltration is carried out at pH 6.5 and at 20°C, and under a pressure of 40 bars, and during the

- 110 permeation the permeate obtained is replaced by water. The average filtration flow rate I is 850 l/m²d.

The dyestuff solution is then concentrated up to a solids content of 6% (I=825 l/m²d) and again

- 115 subjected to diafiltration with 100 kg of water (I=800 l/m²d).

- 2.16 kg of a reaction product of triethanolamine and ethylene oxide, which has an average molecular weight of 1,080 and is adjusted to pH 3 with HCl, are added to this solution, which contains <0.1% by weight of NaCl, relative to the dyestuff. The mixture is then subjected to diafiltration with 100 l of water (I=1,000 l/m²d).

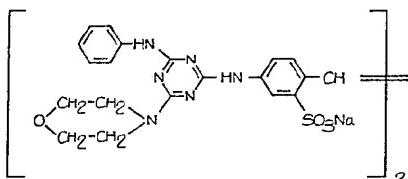
After subsequent concentration, 9 kg of a

stable dyestuff solution with a solids content of 25% and a sodium chloride content of less than 0.1% by weight, relative to the dyestuff, is obtained.

5 Stable, highly concentrated dyestuff solutions are obtained under approximately the same conditions using Direct Yellow 50 (Color Index 29,025) and Direct Orange 49 (Color Index 29,050).

10 Example 2

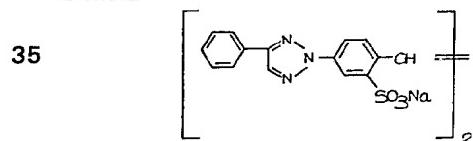
40 kg of a 3.4% strength solution of the brightener of the formula



which contains 200% by weight of sodium chloride, relative to the brightener, are desalinated with 240 kg of distilled water. Using the same apparatus, the same membrane and the same experimental conditions with respect to pressure and temperature as in Example 1, a filtration flow rate of $I=350 \text{ l/m}^2\text{d}$ is achieved. 1,620 g of the amine from Example 1, also adjusted to pH 3 with HCl, are then added to this solution. This solution is again subjected to diafiltration with 50 kg of distilled water $I=350 \text{ l/m}^2\text{d}$. The solution of the brightener which has undergone salt-to-salt conversion is then concentrated ($I=230 \text{ l/m}^2\text{d}$).

10 kg of a stable solution which contains 16% of the amine salt of the brightener and has an NaCl content of less than 0.1% by weight, relative to the brightener, are obtained.

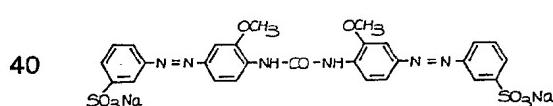
A stable highly concentrated solution is likewise obtained from the brightener of the formula



under approximately the same conditions.

Example 3

50 kg of the solution obtained after the preparation of the dyestuff of the formula



with a solids content of 3% and a sodium chloride content of 120% by weight, relative to the dyestuff, is subjected to diafiltration with 100 kg of water on a reverse osmosis pilot plant apparatus which has a membrane area of 0.36 m^2 and is fitted with a cellulose acetate membrane with a nominal separation limit of MW 500 and a sodium chloride retention of 30%. The diafiltration is carried out at pH 6.5 and at 20°C ,

50 and under a pressure of 40 bars, and during the permeation the permeate obtained is replaced by water. The average filtration flow rate I is $850 \text{ l/m}^2\text{d}$.

The dyestuff solution is then concentrated up to a solids content of 6% ($I=825 \text{ l/m}^2\text{d}$) and again subjected to diafiltration with 100 kg of water ($I=800 \text{ l/m}^2\text{d}$).

530 g of tris-(2-(2-hydroxyethoxy)-ethyl)-amine, adjusted to pH 3 with HCl, is added, for the purpose of salt-to-salt conversion, to this solution, which contains <0.1% by weight of sodium chloride, relative to the dyestuff. The mixture is then again subjected to diafiltration with 75 l of water ($I=1,000 \text{ l/m}^2\text{d}$).

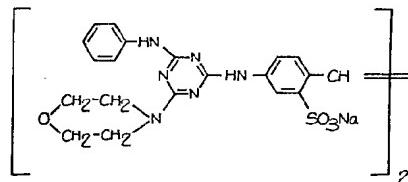
65 This salt-to-salt conversion operation is repeated twice more.

After subsequent concentration ($I=450 \text{ l/m}^2\text{d}$), 8.5 kg of a stable dyestuff solution with a solids content of 20% and a sodium chloride content of less than 0.1% by weight, relative to the dyestuff, are obtained.

Stable, highly concentrated dyestuff solutions are obtained under approximately the same conditions using Direct Yellow 50 (Color Index 29,025) and Direct Orange 49 (Colour Index 29,050).

Example 4

4.3 kg of triethanolamine and 0.75 kg of concentrated HCl are added to 40 kg of a 3.4% strength solution of the brightener of the formula



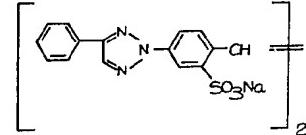
which contains 200% by weight of sodium chloride, relative to the brightener.

The resulting solution is subjected to diafiltration with 90 kg of an aqueous solution containing 8.6 kg of triethanolamine and 1.5 kg of concentrated HCl using the same apparatus, the same membrane and the same experimental conditions with respect to pressure and temperature as in Example 1. The filtration flow rate I is $350 \text{ l/m}^2\text{d}$.

The solution of the brightener which has undergone salt-to-salt conversion is then concentrated ($I=230 \text{ l/m}^2\text{d}$).

95 9.7 kg of a stable solution which contains 16% of the triethanolamine salt of the brightener and has a sodium chloride content of less than 0.1% by weight, relative to the dyestuff, are obtained.

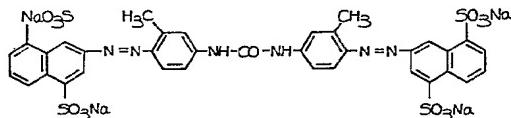
A stable highly concentrated solution is likewise obtained from the brightener of the formula



under approximately the same conditions.

Example 5

10 kg of the press-cake of the dyestuff of the formula



- 5 are dissolved with water to give 50 kg of a 10% strength solution. The dry dyestuff contains 14.6% of Na (ascertained by a residual ash determination).
This solution is subjected to a diafiltration at
 - 10 30°C and under a pressure of 40 bars on a reverse osmosis pilot plant apparatus which has a membrane area of 0.36 m² and is fitted with a membrane of a synthetic polymer, with a molecular separation limit of MW 300 and a
 - 15 sodium chloride retention of 5—10%. Diafiltration is first carried out with 150 l of water, the dyestuff solution being kept at pH 4—5 with dilute hydrochloric acid. Diafiltration is then again carried out with 150 l of water, but the pH value
 - 20 is increased to pH 3 and kept at this value during the diafiltration.

After 75 l of the second part of the diafiltration, 250 g of tris-2-[(2-hydroxyethoxy)ethyl]-amine are added for the purpose of salt-to-salt

- 25 conversion.

A filtration flow rate of $I=1,400 \text{ l/m}^2\text{d}$ is achieved over the entire diafiltration.

After the diafiltration, the 50 kg of dyestuff solution present are concentrated. A further 500 g of tris-[2-(2-hydroxyethoxy)-ethyl]-amine are added during the concentration.

30 After the concentration ($I=500 \text{ l/m}^2\text{d}$), 15 kg of a stable dyestuff solution with a solids content of 29% and a Na content (ascertained by a residual ash determination) of 1.8% are obtained.

Claims

1. A process for the production of a concentrated aqueous solution (as hereinbefore defined) of a dyestuff or of a brightener, inorganic salts being separated off and sodium salt, potassium salt or alkaline earth metal salt of the dyestuff or brightener in the case of anionic dyestuff or brightener, and chloride, sulphate or methosulphate in the case of cationic dyestuff or brightener being converted into a salt which is more readily soluble, without the free acids or bases being intermediately isolated, in which the inorganic salt is separated off by means of a membrane separation process, and, before during or after separating off the inorganic salt originally present, 10 to 500 mol%, relative to the dyestuff, of an ionic compound is added, in which the ionic compound is an ammonium salt of the general formula



in which

R¹, R², R³ and R⁴ independently denote a hydrogen or an alkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl, —(C₂H₄O)_n—H, —(C₂H₄O)_n—H—[CH₂—CH(CH₂OH)_n]—H,

- 60 —(C₃H₆O)_n—H, —[CH₂—CH(CH₂OH)O]_n—H
 or —[CH₂—CH(CH₂OH)—CH₂O]_n—H group
 or two of the radicals R¹, R², R³, and R⁴,
 together with the N atom and optionally
 further hetero-atoms, denote a saturated
 heterocyclic ring, alkyl or alkoxy containing
 1 to 20 carbon atoms,
n is an integer from 2 to 20 and
 X[⊖] denotes the anion of an inorganic acid or
 OH[⊖], or a lithium salt, in the case of an
 anionic dyestuff or brightener, and the ionic
 compound is a salt of a cyclic or acyclic
 organic acid containing, as the cation, the
 cation of an inorganic base, in the case of a
 cationic dyestuff or brightener.

70 2. A process according to Claim 1, in which
 the membrane separation process is reverse
 osmosis, ultrafiltration, dialysis, electrodialysis or
 electroosmosis.

3. A process according to Claim 1 or 2, in which the ionic compound is added after removal of the inorganic salts originally present.

4. A process according to any of the foregoing

- claims, in which the removal of the inorganic salts originally present is carried out at pH 1 to 5 in the case of an anionic dyestuff or brightener and at pH 9 to 13 in the case of a cationic dyestuff or brightener.

5. A process according to any of the foregoing

- claims, in which the ammonium salt of the
90 formula (I) has a molecular weight the same or greater than the molecular weight of the anionic dyestuff or brightener and/or is predominantly held back by the membrane used.

6. A process according to any of Claims 1 to 4,
95 in which the ionic compound in the case of a
cationic dyestuff or brightener is an inorganic salt
of an aliphatic or aromatic monocarboxylic or
polycarboxylic acid or a monosulphonic or
polysulphonic acid which is optionally substituted
100 by hydroxyl, halogen, C₁ to C₄ alkoxy, nitro,
amino, C₁ to C₄ alkyl in the case of an aromatic

- 105 amino, C₁ to C₄ alkyl (in the case of an aromatic acid), cyano or oxo, or is a CH-acid compound.

- 110 8. A process according to Claim 1, when carried out substantially as described in any one of the Examples.

110 9. A concentrated aqueous solution (as hereinbefore defined) when produced by the

process of any of the foregoing claims.

10. A process for dyeing a natural or synthetic fibre material, comprising treating the material with a concentrated aqueous solution as claimed in Claim 9.

11. A process according to Claim 10, in which the material is paper.

12. A natural or synthetic fibre material when dyed by the process of Claim 10 or 11.

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